COMPARISON OF TWO DIFFERENT APPROACHES FOR ENHANCEMENT OF CO₂ REMOVAL BY ADSORPTION ON CARBONS

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Introduction

It is widely believed that emissions from the combustion of fossil fuels are contributing to a rise in the concentration of CO_2 in the atmosphere, which in turn has raised concerns that these CO_2 emissions may be causing global warming. Consequently, CO_2 capture has recently received much attention as a potential means of mitigating fossil fuel CO_2 emissions with adsorption in particular considered to be one of the most promising methods. Activated carbons are well known as adsorbents of gases and vapors. Although the textural properties of the adsorbent plays a key role in the adsorbate/adsorbent interactions, other features such as surface chemistry should also be taken into consideration[1].

The surface chemistry of activated carbon is governed by the presence of heteroatoms such as oxygen, nitrogen, etc. Sometimes the original chemistry of the activated carbon surface is not potent enough to enhance the specific adsorbate-adsorbent interactions or catalytic processes. In such cases the surface chemistry can be modified by the impregnation of an appropriate reagent. Alternatively, modifications can be engendered by the alteration of the surface chemistry of the carbon matrix via the incorporation of heteroatoms.

In this study, two different approaches of developing CO_2 adsorbents are compared. Firstly, the modification of the surface chemistry of carbon concentrates from fly ash (PFA) with a series of nitrogen-containing reagents. Secondly, a range of high nitrogen content carbon matrix adsorbents have been developed by the carbonisation and subsequent activation of a series of sugar and N-compound mixtures. The results of both approaches for developing CO_2 adsorbents will be discussed comparing both the adsorption capacity versus temperature and the ease of regeneration of the different adsorbents.

Experimental

Materials. For the first approach the substrates comprise a high surface area (HS1) and two low surface area (LS1 and LS2) activated PFA-derived unburned carbon concentrates (PFA_ACC). The PFA_ACCs were steam activated in a vertical tube fixed bed furnace. This involved heating these in a stream of nitrogen to 800-850°C, whereupon steam was introduced for a set time interval while the furnace temperature was kept constant. For the impregnation of the substrates, three amines were used, namely poly-ethylenimine (PEI), di-ethanolamine (DEA) and tetra-ethylene-penta-amine-acrylonitrile (TEPAN). DEA and PEI were obtained from chemical suppliers, with both a low molecular mass (mm) and a high mm form of PEI being used, their mms being 600 and 1800 respectively. TEPAN was produced in the laboratory in accordance with a method devised by Birbara, *et al.* [2]. The amine impregnation method was based on that used by Xu, *et al.* [3], and the amine loadings are expressed as a percentage of the sum total of the amine and substrate mass.

For the second approach used in this work, common sugar was used as the carbon matrix source for the adsorbents obtained. The nitrogen source comprised a series of nitrogen compounds with different nitrogen functionalities (i.e., acridine, proline, carbazole and urea), which were supplied by Fisher. In order to increase the char yield, prior to the carbonisation process the mixtures at 50 wt% were pre-treated with sulphuric acid. The carbonisation step was performed by heating the samples in a closed reactor at 10°C min⁻¹ up to 400°C under an inert atmosphere. The products of carbonisation were then activated with CO_2 (100 mL min⁻¹) for 0.5 hours at 900°C. The final adsorbents obtained after the activation step were denoted as MTA, MTC, MTP and MTU, corresponding to the pre-treated mixtures of sugar with acridine, carbazole, proline and urea, respectively.

Characterisation. The surface area, meso- and micro- pore volumes and average pore diameter of the substrates were calculated from N_2 adsorption and desorption isotherms obtained at -196°C using a Micromeritics ASAP 2010 unit. The carbon and nitrogen content of the substrates and sorbents were determined using a using a Carlo Erba NA1500 elemental Analyzer. The thermal stability of the substrates was measured by heating them at a rate of 15°C/min in a Perkin-Elmer thermogravimetric analyzer (tga) from room temperature to 800°C in a stream of nitrogen.

The CO_2 adsorption capacity of the prepared sorbents, which is expressed as the percentage of CO_2 adsorbed by mass of the sorbent (on a dry basis), was measured using the tga. For the isothermal (75°C) tests, approximately 10 mg of the sample were placed into an alumina crucible and dried at 100°C for 30 minutes under a flow of N_2 gas. The temperature was then decreased to 75°C and the gas flow, whilst being kept at a steady flow rate of 20 ml min⁻¹, was shifted from N_2 to CO_2. After 40 minutes, the gas flow reverted to N_2 while the temperature was maintained at 75°C. The temperature-programmed CO_2 adsorption test differed from the isothermal CO_2 adsorption test in that subsequent to the drying stage, the temperature was decreased to 25°C, following which the N_2 gas flow was switched to CO_2. These operating conditions were maintained for 2 h, after which time the temperature was increased at 0.25°C min⁻¹ up to 100°C. Once the sample reached the final temperature (100°C), the gas flow was reverted to to N_2 while the temperature was maintained at 100°C.

Results and Discussion

CO_2 adsorption at 75°C: Influence of amine and substrate. Table 1 lists the activation conditions and pore structure properties of the substrates. Figure 1 below displays the adsorption capacity at 75°C of the amine-impregnated forms of LS1 and LS2.
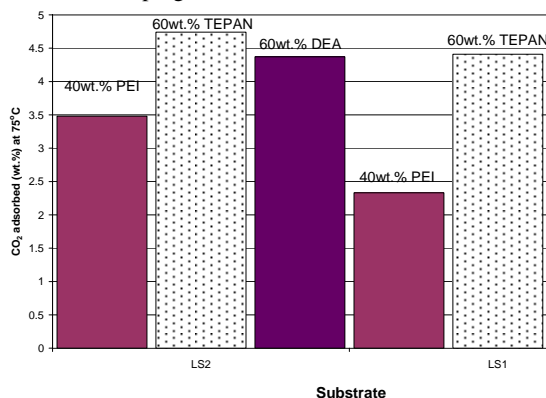

Figure 1. CO_2 uptake of impregnated substrates at 75°C

Of the three amines studied, TEPAN yielded the highest CO_2 uptake. The optimum loading of PEI upon the PFA_ACCs, which was 40 wt.%, at a temperature of 75°C, yielded a CO_2 uptake of approximately 3.5 wt.% whereas the highest CO_2 uptake achieved with the same PFA_ACC (LS2) loaded with the optimum loading of TEPAN (60wt.%) was 4.7wt.%. The CO_2 uptakes reported here

compare to those of ca. 10-12 wt.% with PEI impregnated on MCM-41[3] and on a series of mesoporous silicas which will be reported elsewhere.

Table 1. Textural characteristics and activation conditions of substrates

Sample name	Substrate name	Activation temp (°C)	Activation time (hrs)	Burnout of carbon (wt.%)	BET surface area (m²/g)	Average pore diameter (nm)	BJH ave pore diameter (nm)	Cumulative BJH Pore Volume of mesopores (cm³/g)	Cumulative BJH mesopore surface area (m²/g)
Columbian PFA_ACC	HS1	800	7	55	472.1	2.9	4.7	0.160	136.3
High Marnham	LS2	850	2	43.8	127.0	3.9	5.4	0.102	75.0
PFA_ACC	LS1	800	7	53.92	166.46	4.3	5.4	0.160	118.6

Generally, the highest uptake of CO_2 by mass of amine would be expected to be achieved by PEI, owing to its greater ratio of CO_2-attracting amine groups to carbons; for TEPAN and DEA the amine to carbon ratio is ca. 1:4, whereas for PEI it is 1:2. However, whereas a PEI loading of 40 wt.% produced the optimum CO_2 uptake upon the PFA_ACCs, the same PFA_ACCs dosed with TEPAN yielded the optimum CO_2 uptake at a loading of 60 wt.%. This tallies with TEPAN's low mm – 311[4], as opposed to 1800 for PEI. The lower mm of the TEPAN molecule should enable it to achieve better penetration of the substrate and hence the substrate should be able to accommodate more TEPAN than PEI. The hypothesis that TEPAN's lower mm causes it to have better penetration properties than PEI is corroborated by the fact that the highest CO_2 uptake attained at 75°C using the PFA_ACCs (4.7 wt.%), was achieved with TEPAN.

Influence of PEI mm. Investigations were conducted to ascertain whether a lower molecular mass PEI might prove more effective in elevating the CO_2 adsorption capacity of PFA_ACCs. The results of this work are displayed in Figure 2.
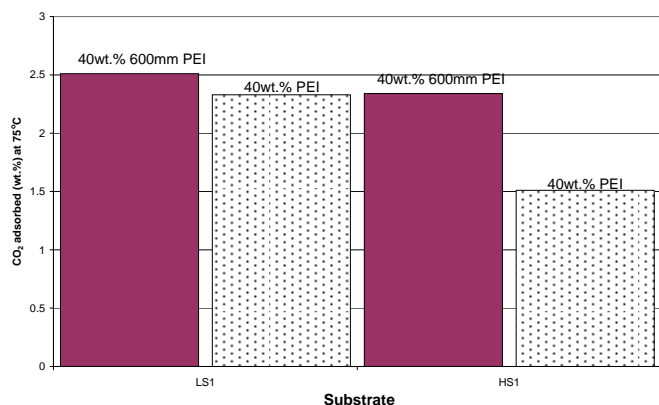

Figure 2. Comparison of CO_2 uptake of substrates impregnated with PEI of mm 600 and 1800 respectively at 75°C

Figure 2 shows that overall PEI 600mm only produces a significant improvement in the performance of HS1. However, it is worth noting that the 600mm PEI molecule has a mm that is nearly double that of TEPAN, therefore its mm might still prove prohibitive in facilitating high penetration of low mesoporosity substrates. What is also interesting to note from Figures 1 and 2 is that PFA_ACC LS2, despite, as shown in Table 1, having a considerably lower

mesopore volume and surface area and than either LS1 or HS1, has a far higher uptake of CO_2 when impregnated with a PEI (1800mm) loading of 40wt.% (3.5wt.%, as opposed to 2.3wt.% and 1.5wt.% for LS1 and HS1 respectively). Potential explanations for this behaviour include its lower burnout of carbon and hence its higher ratio of unburned carbon to ash and additionally its higher activation temperature and the attendant alterations in its pore structure that this might engender.

Thermal stability. The thermal stability of PEI (1800mm), DEA and TEPAN was analyzed. A broad correlation between the temperatures at which the amines began to exhibit a high rate of evolution and their mms was found. These temperatures were ca. 320°C, 225°C and 185°C for PEI, TEPAN and DEA respectively. The thermal stability of these amines was found to drop when they were impregnated in substrates. The diminished temperature evolution is attributable to the fact that the amines are present as a film on the substrates, rather than being in a bulk form, thus increasing their surface area and hence susceptibility to evolution on heating.

CO_2 adsorption of sugar-derived nitrogen enriched carbons. According to the results presented in Table 2 it can be said that carbazole is the N-compound that incorporates the least amount of nitrogen into the carbon, while urea yields the highest nitrogen-containing adsorbent.

Table 2. Chemical Characteristics of the Adsorbents Studied

Sample	N (wt%)	C (wt%)	C/N ratio
MTA	3.9	76.0	0.04
MTC	2.3	81.0	0.02
MTP	3.4	74.9	0.04
MTU	6.3	76.8	0.07

The adsorption capacities of the adsorbents studied are plotted against temperature in Figure 3. In Figure 3a the CO_2 adsorption capacity is expressed as the percentage of CO_2 adsorbed by mass of the sorbent. For these N-enriched carbons the highest adsorption capacity (i.e., highest weight uptake) occurs at room temperature, and a clear decrease is observed as the temperature increases. Furthermore, the process seems to be totally reversible, as the adsorbents reach the initial weight after switching the reactive gas (i.e., CO_2) to N_2 at 100°C. In order to get a clearer picture of the N content effect, the adsorption capacities of these N-enriched carbons were normalised with respect to the BET surface area, taking into account the great influence of this parameter on the CO_2 capture performance of the sorbents. Thus, the weight uptake during the temperature-programmed CO_2 adsorption tests was normalised by the surface area of the adsorbent and the initial mass of the sample, giving a new parameter denoted as W_S. The W_S profiles versus temperature are shown in Figure 3b. It is worth noting that in terms of W_S, the sample with the highest content of nitrogen (i.e., MTU) has the lowest adsorption capacity and the sample obtained by co-pyrolysis with carbazole, MTC, although possessing a comparatively low nitrogen content (see Table 2), has the highest CO_2 adsorption capacity. This indicates that it is not just the amount of nitrogen in the adsorbent, but also the nitrogen functionality that has a strong influence upon the performance of the carbons.
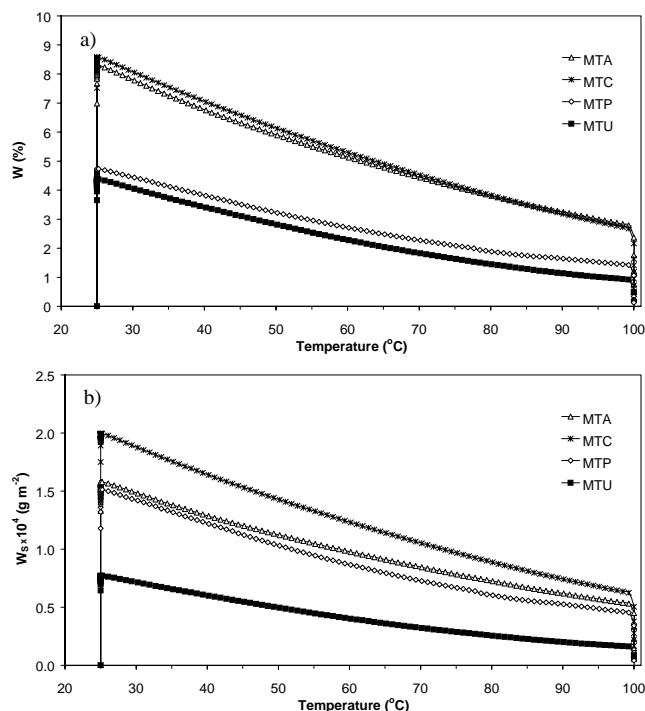
Figure 3. CO_2 adsorption capacities measured during temperature-programmed adsorption/desorption tests of the N-enriched carbons studied

In comparison to the amine-loaded substrates, the N-enriched carbons perform better than the PFA_ACCs. Further work is intended in order to see how the performance of these adsorbents may be improved and furthermore how the substrates perform over a period of multiple adsorption/regeneration cycles.

Conclusions

CO_2 adsorptions have been successfully prepared by impregnating amines upon PFA_ACCs and through the carbonization and subsequent activation of mixtures of sugar and nitrogen containing compounds. For the PFA_ACCs, TEPAN was a stronger CO_2 adsorption enhancing amine than DEA or PEI. Of the N-compounds mixed with the sugars, urea yielded the highest nitrogen content in the resulting carbons but carbazole, despite yielding the lowest nitrogen content, engendered the highest adsorption capacity both in terms of the overall amount of CO_2 adsorbed by the sorbents and also the mass of CO_2 adsorbed per m^2 of their surface area. This indicates that it is not just the amount of nitrogen in the adsorbent, but also the nitrogen functionality that has a strong influence upon the performance of the carbons.

References

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